

ZERO PRESSURE JOULE-THOMSON COEFFICIENT FOR A FEW NON-POLAR GASES ON THE MORSE POTENTIAL

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Recently Konowalow, Taylor and Hirschfelder (1960, 1961) have added the Morse potential to the list of potentials for which detailed computations of various gas properties are possible. This potential is

$$\phi(r) = \epsilon(x^2 - 2x),$$

where

$$x = \exp [-(c/\sigma)(r - r_m)].$$

Here, $\phi(r)$ is the potential energy between two molecules at a separation distance r , ϵ is the depth of the potential minimum at $r = r_m$, σ is that value of r for which $\phi(r) = 0$, and c is a third parameter which governs the curvature at the minimum and the steepness of the repulsive limb. Konowalow and Hirschfelder (1961) have determined the three parameters for a few non-polar gases from crystal and second virial data. They also compared the experimental second virial values with the calculated values according to this potential and the exp-6 and Lennard-Jones (12-6) potentials. This work revealed that most probably the Morse and exp-6 potentials are comparable in accuracy and both are somewhat superior to the 12-6 potential. Saxena and Gambhir (1963) have also investigated the second virial data of a few pure gases over a wider temperature range, and also of a few gas mixtures. They found the Morse potential to be somewhat superior to the other two potentials. Saxena and Bahethi (1963) have calculated the transport properties in conjunction with the potential parameters given by Konowalow and Hirschfelder (1961) and compared the values with the experimental data. They found that the transport properties are not adequately reproduced and have expressed the necessity of redetermination of the parameters for an accurate relative assessment.

To investigate the adequacy of this potential further we consider the experimental data of zero pressure Joule-Thomson coefficient, μ^0 . The theoretical computed values of the reduced μ^0 are given by Konowalow, Taylor and Hirschfelder (1960). The experimental values of $\mu^0 C_p^0$ (C_p^0 being the zero pressure specific heat of the gas at constant pressure) for He, Ar, CH₄, and N₂ have been reported by Lunbeck (1950). In addition to these values we also consider the experimental

data of Budenholzer, Sage and Lacey (1939) for CH_4 ; and of Charnley, Isles and Towley (1953), Roebuck and Osterberg (1935), Gusak (1937), and Collins and Keyes (1939), (as reported by Charnley *et al.* 1953) for N_2 . These experimental values are shown plotted in Fig. 1. The computed values both according to the Morse as well as the $L-J$ (12-6) potentials are also shown. The exp-6 potential could not be considered for the theoretical values of the reduced μ^0 are not available. We also do not consider here the $L-J$ (18-6) potential introduced by Saxena and Joshi (1962) because though the reduced μ^0 is known, potential parameters for most of these gases have not been determined as yet. The potential parameters used in calculations are those tabulated by Konowalow and Hirschfelder (1961) except for He. It may be noted that for both the potentials the parameters have been determined from the equilibrium properties only. For He we use the parameters of Bahethi and Saxena (1963) determined from the second virial data. These are $\epsilon/k = 4$, $\epsilon/k = 14.43^\circ\text{K}$, and $\sigma = 2.976\text{\AA}$.

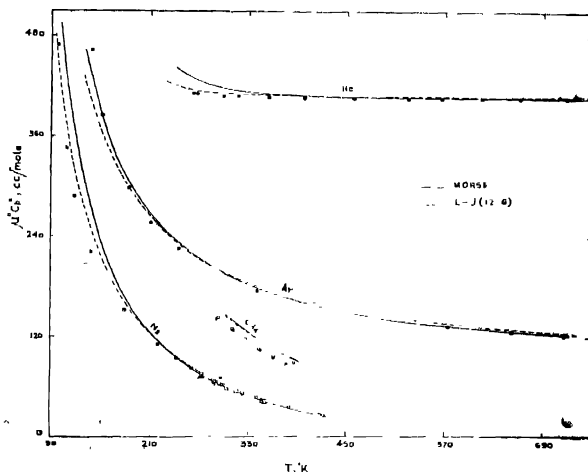


Fig. 1. Plots of $\mu^\circ C_p$ as a function of temperature. For Ar ordinates have been displaced by +120 units, and for He abscissae and ordinates have been displaced by +180 and +420 units, respectively. Experimental data: He, Ar, CH_4 , N_2 , \bullet Lumbeck; CH_4 , \circ Budenholzer *et al.*; N_2 , \circ Charnley *et al.*, Δ Gusak, ∇ Roebuck and Osterberg, \square Collins and Keyes.

From the figure we find that for Ar the Morse potential is better than the 12-6 potential over the entire temperature range. For N_2 at high temperatures both the potentials are about equally good but the differences are appreciable at low temperatures. The deviations, however, are less for the 12-6 potential. For CH_4 both the potentials yield approximately similar results, with a slight preference

for the 12-6 potential. Some alternative choices for the 12-6 potential parameters are also available for this gas. Schamp *et al.* (1958) have reported the potential parameters for CH_4 ($\epsilon/k = 148.07^\circ\text{K}$, $\sigma = 3.810\text{\AA}$) from the analysis of their virial data. These parameters lead to values which are nearly 4% greater than those plotted in the figure. Similar results are obtained if we consider the potential parameters given by Hamann and Lambert (1954) for CH_4 .

In the case of He the 12-6 potential is definitely superior to the Morse potential in the low temperature range even if the quantum corrections are considered. Bahethi and Saxena (1963) have also noted that for He the above parameters completely fail to reproduce the transport properties. They have determined the Morse potential parameters from viscosity data also. The values are $\epsilon = 6$, $\epsilon/k = 8.55^\circ\text{K}$, and $\sigma = 2.687\text{\AA}$. These parameters reproduce the transport properties but fail in the case of second virial coefficient. If we use these parameters to compute $\mu^0 C_p^0$ we get almost the same values at high temperatures but consistently smaller values at low temperatures. This disagreement will further increase if quantum corrections are applied.

The above comparison leads to the conclusion that the $L-J$ (12-6) potential is slightly better than the Morse potential. This conclusion is specially interesting in view of the simplicity of the 12-6 potential. The fact that in the case of He one set of Morse parameters cannot correlate both the equilibrium and non-equilibrium properties implies that the Morse potential is not as good as the other two potentials, viz. 12-6 and ex-6, for this gas.

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